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PERFORMANCE MAPPING STUDIES IN REDOX FLOW CELLS

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ABSTRACT

Pumping power requirements in any flow battery system constitute a direct parasitic energy loss. It is therefore useful to determine the practical lower limit for reactant flow rates. Through the use of a theoretical framework based on electrochemical first principles, two different experimental "flow mapping" techniques are developed to evaluate and compare electrodes as a function of flow rate. For the carbon felt electrodes presently used in NASA-Lewis Redox cells, a flow rate 1.5 times greater than the stoichiometric rate seems to be the required minimum.

SUMMARY

The NASA-Redox energy storage system, which falls into the general class of flow batteries, employs pumps to circulate reactants from storage tanks, through the flow cells where the electrochemical reactions take place, and back. Thus, there is concern for the magnitude of the pumping power requirements, which represent a parasitic energy loss. The goal in Redox system design is to reduce the pumping power as much as possible while still maintaining adequate cell and stack performance.

Two different "flow mapping" techniques, both incorporating a theoretical framework based on electrochemical first principles as a standard of comparison, were used to determine minimum adequate flow rates. The first method considers performance at various constant currents over a range of flow rates for a fixed state-of-charge. The second method involves a constant current discharge at a fixed multiple of the stoichiometric flow rate with varying state-of-charge. Both methods are useful, and indicate the minimum acceptable reactant flow rate for the present NASA-Lewis electrode configuration is about 1.5 times the stoichiometric flow requirement.

INTRODUCTION

The NASA-Redox Energy Storage System (ref. 1,2) is based on the continuous flow of two soluble electrolytic reactant solutions, each from a separate storage tank, through a power conversion section of flow cells. Each individual cell is composed of several components which form two paired half-cells. (See fig. 1.) The electrochemical reactions in the cell take place at the surface of the porous carbon felt electrodes. Each felt electrode is enclosed within a flow field frame assembly that is bounded by a bipolar plate on one side and a common anion exchange membrane separating the two half-cells on the other. Electrolyte enters the flow field from the inlet primary manifold, then flows up through the inlet port and into the inlet secondary manifold. (See fig. 2.) Here the flow is distributed along the width of the half-cell before moving evenly upward in sheet flow fashion through the porous carbon felt electrode. Flow then enters the exit secondary manifold before leaving the half-cell through the exit port and finally the exit primary manifold. In stacks of Redox cells, adjacent cells are separated by common bipolar plates.

Inlet and outlet primary manifolds run the length of the stack, supplying parallel flow to all cells.

Pumping power requirements are inherent with flow of the reactant solutions, and are manifested as a direct parasitic energy loss to the Redox system. Maintaining satisfactory cell and stack performance while minimizing the flow rate reduces this parasitic energy loss. The task at hand is thus to determine the minimum acceptable flow rate for various electrodes by evaluating their performance characteristics over a range of flow rates. This is accomplished by first establishing a theoretical framework based on electrochemical first principles and then using either of two different "flow mapping" techniques to compare the performance of the various electrodes relative to the theoretical framework. This approach provides a methodology for selecting the electrode having the best performance characteristics at the lowest required flow rate.

FLOW CONSIDERATIONS

The necessary flow for adequate performance in a Redox flow cell depends on several factors. These include solution state-of-charge, cell operating current, and total solution concentration. Stoichiometric flow is defined as that flow rate at which the electrolyte is totally depleted of the active ionic species just as it leaves the cell. This is the theoretical minimum flow required for adequate cell performance. Flow rates greater than this value are expressed as multiples of the stoichiometric flow rate.

One molar electrolytic solutions of iron chloride and chromium chloride each contain $1.608 \frac{\text{amp.} \cdot \text{min}}{\text{cm}^3}$ capacity when fully charged. This capacity, when related to the specified current (I) and solution state-of-charge (SOC), forms the following relationship for stoichiometric flow (F_{SF}):

$$F_{SF} = \frac{I}{1.608 \times \text{SOC}} \frac{\text{cm}^3}{\text{min}} \quad (1)$$

where current is in amps, and state-of-charge is a dimensionless value. It is apparent from this relationship that stoichiometric flow requirements increase as the state-of-charge decreases, for a constant current requirement. Thus, the stoichiometric flow requirements of a cell at constant current are continually changing as the electrolytes cycle between a fully charged and fully discharged state.

When operating under constant flow and current conditions, the stoichiometric flow multiple decreases as the SOC decreases, and cell performance will decline as the stoichiometric flow multiple approaches unity and concentration polarizations become significant. It is the purpose of this paper to develop a method for electrode evaluation based on cell performance and flow rate characteristics.

MASS TRANSPORT EVALUATION PROCEDURES

An evaluation procedure was desired that would map the performance of a cell as the flow rates were reduced toward the point at which mass transport phenomena became the significant limiting factors of cell performance. With the SOC and current held constant as the flow rates are decreased, the mathematically defined stoichiometric flow rate is approached with a concurrent

decline in cell performance. A rapid, total performance loss occurs when the flow rate is less than stoichiometric. Any evaluation technique of flow effects should attempt to separate reduced cell performance, caused by IR drops and Nernstian losses, from mass transport phenomena associated with the properties of the electrode and cell design. A partial list of possible causes of poor mass transport characteristics within a cell would include poor catalyst distribution, poor secondary manifold design, uneven distribution of flow within the structure of the sheet flow electrode, large values of the effective fluid film thickness, etc.

CONSTANT CURRENT ELECTRODE EVALUATION

Although some modeling work has been done as it relates to porous electrodes (ref. 3), it was decided to generate an evaluation procedure using Ohm's law, Nernstian type corrections and the mass balance equation for calculating cell outlet conditions knowing inlet conditions, flow rate, and cell current. Figure 3 contains a calculated framework against which we currently compare the performance of single cells in order to estimate mass transport characteristics, and was generated knowing the Redox solutions were of equal concentration (C) such that in each solution $(C_{ox}+C_{red})_A = (C_{ox}+C_{red})_B$ and the solutions were in balance, $(C_{ox})_A = (C_{red})_B$, from an electrochemical state-of-charge point of view. The calculations for this figure were based on using 1.0 Molar chromium and iron solutions at 50% state-of-charge. From experience, the open circuit voltage was taken as 1.05 volts at room temperature. Since no kinetic polarizations are associated with these couples when using properly catalyzed electrodes, the cell voltage at different operating currents, in the absence of concentration polarizations or Nernstian effects, is calculable from an equation of the form

$$E_{cell} = E_{oc} - IR \quad (2)$$

where E_{oc} is the effective cell open circuit voltage for the existing SOC. These values are plotted as horizontal lines, one for each current. I is the operating current and R is the measured cell resistance obtained from a standard polarization curve. Slightly below these lines are the calculated Nernstian corrections which indicate the drop in cell voltage at the lower flow rates caused by the large changes in reactant-to-product concentration ratios between cell inlet and exit. For example, if, for a given current requirement, the flow rate is adjusted to $2.0 \times F_{SF}$ and the cell is at 50% SOC so that $C_{Cr+2, inlet} = 0.5$ M, the exiting reactant concentration would be $C_{Cr+2, exit} = 0.25$ M. Thus the "average" reactant concentration would be

$$C_{Cr+2} = \frac{C_{Cr+2, inlet} + C_{Cr+2, exit}}{2} = \frac{0.50 + 0.25}{2} \text{ M} \quad (3)$$

= 0.375 M, and the "average" product concentration would be $1.0 \text{ M} - 0.375 \text{ M} = 0.625 \text{ M}$. The Nernstian correction to the cell open circuit voltage at 50% SOC is thus

$$\begin{aligned}
-\frac{RT}{nF} \ln \frac{\prod_{i=1}^h [C_{\text{products}}]_h}{\prod_{i=1}^h [C_{\text{reactants}}]_h} &= -\frac{RT}{nF} \ln \frac{(C_{\text{Cr}+3})(C_{\text{Fe}+2})}{(C_{\text{Cr}+2})(C_{\text{Fe}+3})} \\
&= -0.026 \ln \frac{(0.625)^2}{(0.375)^2} = -0.026 \text{ volt} \quad (4)
\end{aligned}$$

where $R = 8.315$ joules/g-mol $^{\circ}\text{K}$, $T = 300^{\circ}\text{K}$, $n = 1\text{eq/g-mol}$, and $F = 96500$ A-sec/eq. For each current and flow rate there is a corresponding concentration change across the cell which necessitates such a voltage correction. As long as the inlet solution concentration remains fixed, it can be seen that a given multiple of stoichiometric flow will result in a specific value of the Nernstian correction which is independent of the current. Equal values of the Nernstian correction for each of the four current levels were joined to plot lines of constant multiples of the stoichiometric flow rate as shown on figure 3.

STOICHIOMETRIC FLOW RATE ELECTRODE EVALUATION

A second type of evaluation procedure was also found to be very helpful. It is similar to the first in that it differentiates the effects caused by IR and Nernstian loss from those caused by mass transport effects within the cell and electrode. The second procedure typically involves the discharge of a cell from 90% to 10% SOC at one particular multiple of the stoichiometric flow rate. This requires continuously increasing the flow rate during discharge.

In figure 4 is plotted the open circuit voltage versus the state-of-charge for the case of 1.0 Molar solutions electrochemically in balance. This open circuit voltage curve is then corrected for the cell internal resistance after which the Nernstian correction is applied for various states-of-charge. For any particular multiple of the stoichiometric flow rate, the Nernstian correction is greatest at higher states-of-charge because the magnitude of the concentration change across the cell is greatest under these conditions.

EXPERIMENTAL SET-UPS AND PROCEDURE

The data for this report were obtained from a two-cell stack with an active electrode area of 929 cm^2 in each cell. Only one cell was operational since the other cell was used to monitor open circuit voltage and hence solution state-of-charge via the Nernstian relationships. Two storage reservoirs were utilized, one containing five liters of acidified chromium chloride solution and the other five liters of acidified iron chloride solution. Two flowmeters, which were calibrated for each solution, measured the flow rate supplied by the centrifugal pumps. Flow rate, cell operating voltage, current, and open circuit voltage were continuously monitored in order to assess cell performance as the system was cycled through various operating conditions. (See fig. 5.)

RESULTS

The data for figure 3 were generated by setting the cell current, flow rate, and state-of-charge of the solutions at selected values. As shown in figure 3, the flow rate can also be expressed as the superficial frontal velocity of the fluid as it proceeds upward through the electrode or as the space velocity of the fluid, which is the reciprocal of the residence time.

These performance maps can be generated at different states-of-charge, but they are not simple translations of figure 3. For example, the change in concentration across a cell for a given multiple of the stoichiometric flow rate is larger the closer the inlet solutions are to being fully charged, thus requiring larger Nernstian voltage corrections. Upon examination of figure 3, it can be seen that the curve including the Nernstian correction and the actual data separate near $1.5 \times F_{SF}$, with the actual data dropping off rapidly as the flow rate is decreased to stoichiometric and beyond. Any point on the curve lying to the right of the sharp downturn, either on or below the Nernstian correction line, is a stable operating point for the cell. Any point to the left of the downturn is unstable and the cell voltage continues to decay. This type of plot is therefore very useful in comparing electrodes and evaluating their performance characteristics. Electrodes with acceptable performance are characterized by actual data curves that separate significantly from the Nernstian correction lines only at low multiples of the stoichiometric flow rate, in this case $1.5 \times F_{SF}$.

Both the Nernstian corrections and the actual data plots show lower cell voltage as flow is decreased. This lower cell voltage yields a lower cell power output for a given current, but also requires less pumping power due to the decreased flow rate. Therefore, an optimum operating point exists where the net available power for a specific operating condition is a maximum.

Figure 4 is typical for the second type of electrode evaluation procedure. Shown are the curves for open circuit voltage, both with and without resistance and Nernstian corrections, and actual data, all as a function of solution state-of-charge. This figure is for a constant current discharge at $2.0 \times F_{SF}$. As in figure 3, the actual data approach very closely the Nernstian correction curve, falling away slightly at the extremes in solution state-of-charge because of mass transport phenomena. Concentration polarization caused by the thick diffusion layer at the electrode surface may occur at the low flow rates that exist at the beginning of discharge. At low flow there may also be poor fluid distribution within the cell. Diffusion limiting conditions caused by the low reactant concentrations and concentration gradients at the end of discharge when the flow rates are substantially higher may also occur. These effects appear to be evident here to some extent; nevertheless, performance is stable throughout the entire discharge.

Figure 6 shows typical performance for an electrode at three different constant current values during discharge. The cell voltage drops continuously, more rapidly at lower states-of-charge. A higher current simply manifests itself in a lower voltage. Plots of this kind can be generated for several different electrodes at the same multiples of the stoichiometric flow rate and compared directly in order to determine the electrode with the best performance. The point at which the actual data and the Nernstian correction curve separate is an additional parameter that aids in the selection of electrodes with acceptable performance characteristics. By varying the multiple of the stoichiometric flow rate, as in figure 7, additional insights can be obtained. Voltage increases as the stoichiometric flow multiple is increased; however, the general shape of the curve remains unchanged. Thus, direct com-

parisons of various electrodes at different multiples of the stoichiometric flow rate can be used to evaluate performance characteristics.

This type of plot can also be used to determine the optimum operating conditions for an electrode to deliver maximum net power. As shown in figure 3, higher stoichiometric flow multiples yield higher cell voltages at constant current, but at the expense of correspondingly higher pumping power requirements. An optimum trade-off will exist between pumping power input and cell power output to deliver the maximum net power for a specific set of operating conditions.

CONCLUDING REMARKS

The NASA-Redox concept is dependent on the flow of soluble electrolytic reactant solutions. This flow necessitates pumping power, which is a direct parasitic loss to the Redox system. Operating at the minimum flow necessary for adequate cell and stack performance reduces the system pumping power requirements.

Two methods for evaluating electrode performance characteristics have been developed, both of which work well. The first method maps the electrode performance for a fixed state-of-charge at various constant currents over a range of flow rates, while the second method involves a constant current discharge at a fixed multiple of the stoichiometric flow rate. The data indicate a minimum stoichiometric flow multiple of $1.5 \times F_{SF}$ is required for adequate cell performance. Below this flow rate, mass transport problems begin to occur.

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3. Trainham, James A.; and Newman, John: A Comparison Between Flow-Through and Flow-By Porous Electrodes for Redox Energy Storage. *Electrochem. acta*, vol. 26, no. 4, 1981, pp. 455-469.

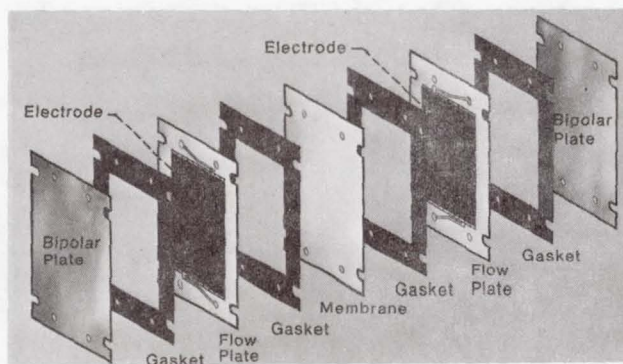


Figure 1. - Redox single cell components.

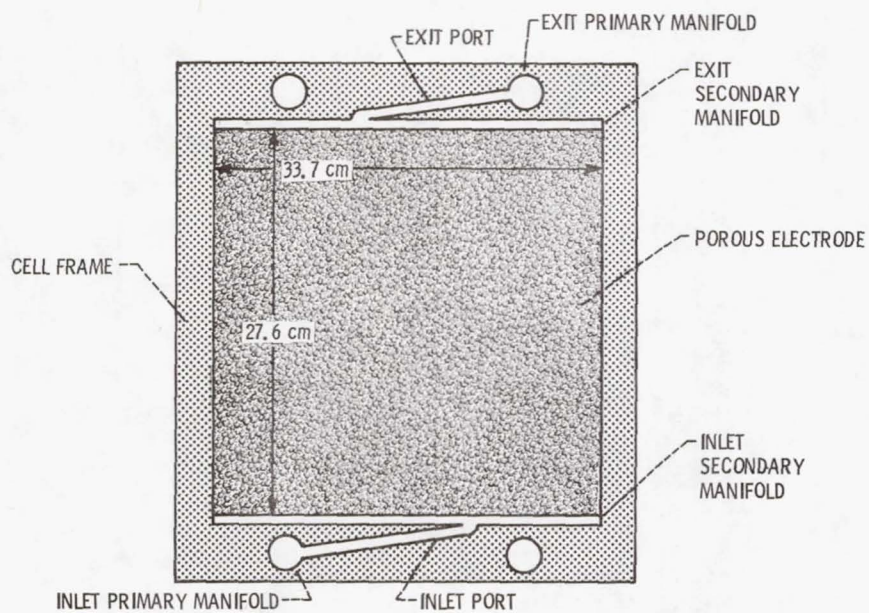


Figure 2. - Planform of half-cell using porous flow through felt electrode.

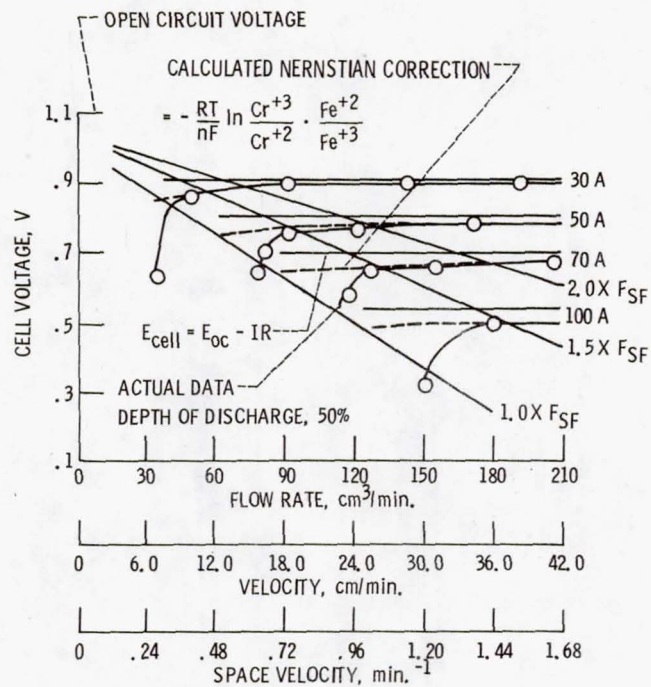


Figure 3. - Performance map of a 929 cm^2 single cell at constant depth of discharge and comparison with theoretical framework.

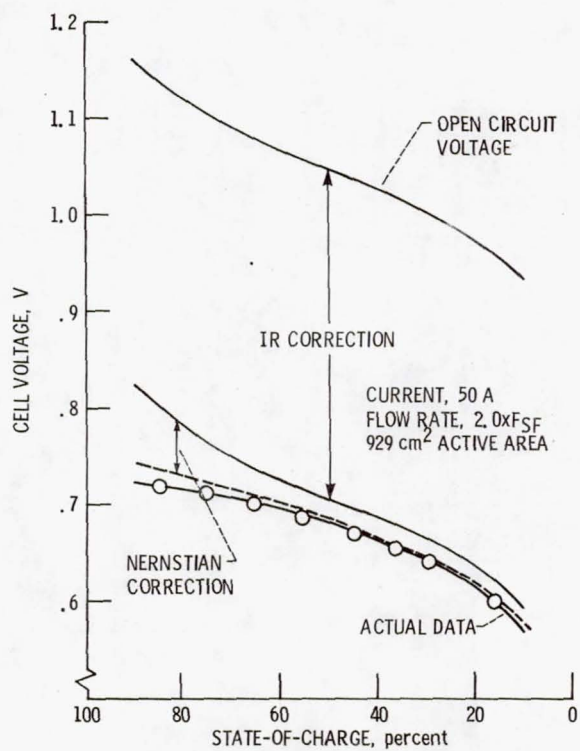


Figure 4. - Performance map of a 929 cm^2 single cell at constant stoichiometric flow multiple and comparison with theoretical framework.

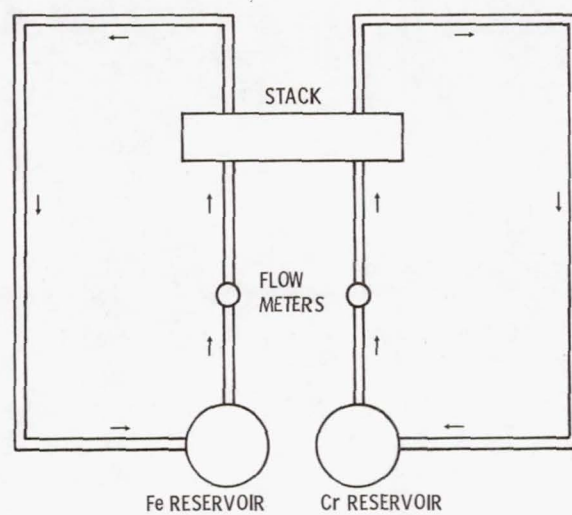


Figure 5. - Plan-view of experimental set-up.

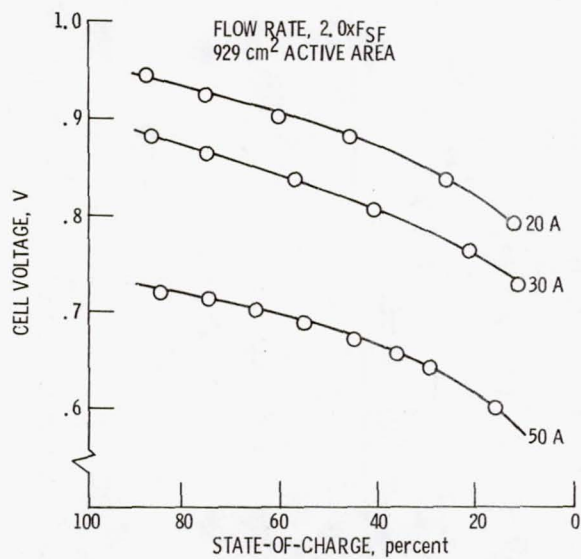


Figure 6. - Performance map of a 929 cm² single cell at several different currents.

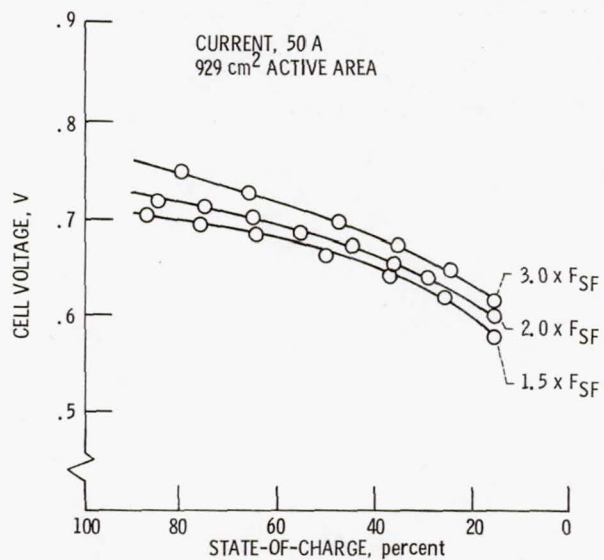


Figure 7. - Performance map of a 929 cm² single cell at several different stoichiometric flow multiples.

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